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Methods and Results of Characterization of Organic Emissions from an Indoor Material

Acurex Corp., Research Triangle Park, NC

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16. ABSTRACT The paper presents the method and example results for determining organic air emissions from a common indoor material (a water-based adhesive). A well instrumented and characterized 0.166 cu m stainless steel test chamber was used to ventilate sample materials at controlled air change rates, temperatures, and relative humidities. The test chamber outlet air stream was sampled using Tenax (1.6 g) filled glass cartridges. The Tenax sample cartridges were then thermally desorbed for further concentration onto a Nutech model 8528 purge-and-trap system and desorption to a packed-column gas chromatograph for analysis. Organic emissions were quantified on species-specific and total-organics bases. Test chamber concentrations of total organics for the adhesive were observed to diminish with time. Calculated emission rates for the adhesive were determined to be 95 micrograms/g/hr after ventilation at 1.77 air changes per hour (ACHs) for 10 hr, and 259 micrograms/g/hr after 24-hr ventilation at 3.6 ACHs. (Copyright (c) Atmospheric Environment 1987.)

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Pollution	Pollution Control	13B
Emission	Stationary Sources	14G 04B
Organic Compounds	Indoor Air	07C
Volatility	Volatile Organics	20M
Adhesives		11A
Ventilation		13A
Temperature		
Humidity		

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METHODS AND RESULTS OF CHARACTERIZATION OF ORGANIC EMISSIONS FROM AN INDOOR MATERIAL

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Abstract—The method and example results for the determination of organic air emissions from a common indoor material are presented. A well instrumented and characterized 0.166-m^3 stainless steel test chamber is used to ventilate sample materials at controlled air change rates, temperature and relative humidity. The test chamber outlet air stream is sampled using Tenax® (1.6 g) filled glass cartridges. The Tenax® sample cartridges are then thermally desorbed for further concentration onto a Nutech® model 8528 purge and trap system and desorption to a packed column gas chromatograph for analysis. Organic emissions are quantified on a species specific basis and total organics basis. Test chamber concentrations of total organics for a water-based adhesive are observed to diminish with time. Calculated emission rates for the floor adhesive were determined to be 95 $\mu g\,g^{-1}\,h^{-1}$ after ventilation at 1.77 air changes per hour for 10 h and 259 $\mu g\,g^{-1}\,h^{-1}$ after 24-h ventilation at 3.6 air changes per hour.

Key word index: Volatile organics, ventilation, temperature, humidity, indoor materials emissions.

INTRODUCTION

In the fall of 1983, the Congress of the United States of America recognized through a special appropriation for the Environmental Protection Agency the need to formally address and develop a comprehensive research program directed at defining and characterizing indoor air quality concerns.

This governmental response can be seen as a direct response to the accumulated evidence (WHO, 1979, 1982; NAS, 1981a, b) of the prevalence and potential health risks associated with common indoor air pollutants such as radon, formaldehyde and other organics, tobacco smoke, combustion gases, microorganisms and allergens.

The current Environmental Protection Agency research strategy (Interagency, 1985) calls for an effort directed at (1) developing an understanding of the magnitude of the risk to human health from exposures to indoor air pollutants, the contribution of various energy conservation measures, and introduction of new building materials and consumer products; and (2) providing technical information and guidance, including cost effective mitigation measures, to State and local governments, the private sector and the general public.

Within this strategy framework and based on the pioneering studies of Mølhave (1979), Girman *et al.* (1984), Andersen *et al.* (1975), Matthews *et al.* (1983) and Pickrell *et al.* (1984), the following source characterization effort, herein reported, was developed.

This paper and companion project papers found in this issue of *Atmospheric Environment* by Dunn and Merrill *et al.* serve to address in specific issues, limitations and recommendations identified in the earlier cited laboratory chamber source characterization studies; viz.,

1. the need to establish techniques for rapid screening of products for organic emissions;
2. the need to establish the effects of aging, sample conditions and conditioning, and sample loading (ratio of sample area to test chamber volume) on emission test results;
3. the need to determine the effects of environmental parameters such as temperature, ventilation, and humidity on organic emission rates; and
4. the need for development and verification of mathematical (emission rate) models to provide a basis for identifying effective source control measures.

APPROACH

The procedures and preliminary results reported here are directed at meeting three objectives which can be accomplished as part of a long-term research program. These objectives are (1) to establish emission factors and estimates of cumulative emissions of

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organics for selected materials and products; (2) to develop general mathematical source emission rate process models suitable for use in health risk assessments; and (3) to identify, through assessments of information from activities directed at meeting (1) and (2), effective source emission control approaches.

Objectives (1) and (2) are directly addressed by the effort presented in this paper. Objective (1), namely the determination of organic emission factors, proceeds directly from application of the mass balance equation to the experimental conditions of each material emission test. For a well-mixed chamber with inlet and outlet air streams, at the same temperature and pressure, the mass balance equation is:

$$V\frac{dC_o}{dt} = EA - L - Q(C_o - C_i) \quad (1)$$

where V = chamber volume [m^3]
C_o = concentration of pollutant in chamber [$mg\,m^{-3}$]
t = time [h]
E = pollutant emission rate [$mg\,m^{-2}\,h^{-1}$]
A = source surface area [m^2]
L = pollutant loss rate in chamber [$mg\,h^{-1}$]
Q = rate of air exchange in chamber [$m^3\,h^{-1}$]
C_i = concentration of pollutant in inlet air [$mg\,m^{-3}$].

Where a material test chamber is made of unreactive material and the inlet air stream has been cleaned of pollutant, L and C_i are zero and the mass balance Equation (1) reduces to

$$V\frac{dC_o}{dt} = EA - QC_o. \quad (2)$$

Integration of Equation (2) yields

$$C_o(t) = \frac{EA}{Q}(1 - e^{-Qt/V}) + C_o(o)e^{-Qt/V} \quad (3)$$

where $C_o(t)$ = chamber concentration of pollutant at time, t[$mg\,m^{-3}$]. At steady state conditions Equation (3) reduces to

$$C_o = \frac{EA}{Q}, \quad (4)$$

and solving for the pollutant emission rate, E, yields

$$E = \frac{QC_o}{A}. \quad (5)$$

Equation (5) permits an accurate calculation of a material's organic emission rate under the conditions of the derivation; viz., no pollutant losses in the chamber, a clean ventilation air supply and steady state conditions. Equation (3) when solved for the emission rate permits estimation of an unsteady state emission rate as characterized by a material sample where the quantity of pollutant effectively available for release is continually being diminished. Its form is

$$E = \frac{Q}{A}\left(\frac{C_o(t) - C_o(o)e^{-Qt/V}}{1 - e^{-Qt/V}}\right) \quad (6)$$

Equation (5) and (6) make explicit the ability of chamber experiments to provide not only steady state emission factors but also estimates of emission factors which change as a function of age. Chamber experiments can be used to develop empirical emission process rate models as a function of sample loading ratios (AV^{-1}), material ventilation (Q), and pollutant concentration (C_o), where measured concentrations are a function of pollutant diffusivity from the source material and mixing in the chamber. Because diffusivity of gases at low density is almost composition independent (Bird *et al.*, 1960), observation of chamber temperatures and concentrations as a surrogate for pollutant partial pressure differentials provides the empirical data set needed to develop a process emission rate model for selected indoor materials.

For materials where the bulk phase of the material itself may be a barrier to pollutant mass transport, as in certain wood products, air humidity may be a significant factor (Andersen *et al.*, 1975; Matthews *et al.*, 1983). Other research (Pickrell *et al.*, 1984), which manipulated numerous other test condition variables, such as sample loading and ventilation rates, may raise questions about the universality of the humidity relationship at least with regard to formaldehyde emissions from wood products. The work of Pickrell *et al.* (1984) suggests a need to identify the interrelationship of numerous test conditions which may affect organic emission rates. The experimental description which follows describes a step in that direction.

EXPERIMENTAL

The U.S. EPA, Air and Energy Engineering Laboratory's Emission Test Facility shown in block diagram form in Fig. 1 was operated in accordance with an Agency required and approved Quality Assurance Project Plan (Radian, 1985). This Plan delineated (1) a mechanical performance appraisal to ensure the Test Facility's ability to maintain emission test chamber environmental conditions of relative humidity, temperature and airflow within acceptance criteria limits and to identify possible environmental control interactions, (2) a test of organic chemical recoveries through the test chamber, and (3) the testing of selected indoor materials to determine their organic emission rate characteristics over time under varying test chamber ventilation conditions.

The Test Facility's clean air generation and delivery are provided by an oil-less compressor drawing in ambient air followed by removal of airstream moisture by a Permapure® membrane dryer and removal of trace organics by catalytic oxidation by two Mine Safety Appliance® model B units in parallel.

The cleaned air flow supplying the test chamber and sample conditioning chamber is then monitored and controlled in parallel streams by two Tylan® mass flow controllers whose performance is monitored on an IBM-PC® monitor and recorded during test runs by a modified Cyborg® software process control package. The cleaned, metered air streams are

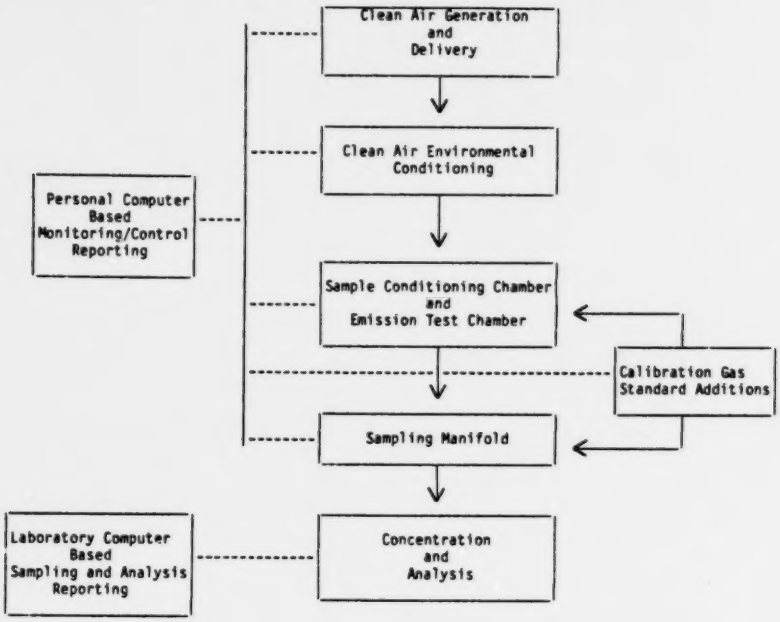
Clean Air Generation and Delivery
Clean Air Environmental Conditioning
Personal Computer Based Monitoring/Control Reporting
Sample Conditioning Chamber and Emission Test Chamber
Calibration Gas Standard Additions
Sampling Manifold
Laboratory Computer Based Sampling and Analysis Reporting
Concentration and Analysis

Fig. 1. Schematic of process flow and automated communications of the AEERL Emission Test Facility.

then supplied with HPLC grade distilled water metered by a model 220 Sage® syringe pump. Airstream temperatures are monitored using Omega® platinum resistance thermometers at the heated water injection point and at the entrance to the Forma Scientific® temperature control incubator which houses coiled inlet air stream lines for inlet in-stream temperature equilibration before delivery to the test and conditioning chambers which are also housed in the Forma® incubator. The emission test chamber (ETC) and sample conditioning chambers are identical in construction, being 55-cm cubes (166.4 ℓ) of 316 stainless steel. Each chamber is fitted with 0.64-cm (1/4-in.) OD inlet and 1.3-cm (1/2-in.) OD outlet ports for stainless steel and glass connections, respectively. Each chamber is fitted with top face ports for a mixing fan, temperature probe and humidity probe, whose monitoring and operations are keyed to the Cyborg® process control software.

Calibration gas may be added to the test chamber or sampling manifold through computer control of three-way solenoid valves that control the calibration gas flow from Metronics® permeation tube calibrators equipped with orifice flow control. Calibration gas was added through the test chamber in tests of organic recoveries and to a mixing flask located between the test chamber and sampling manifold during material emissions testing.

During organic recovery and material emission testing, test chamber air samples were drawn from the sampling manifold onto Tenax® filled glass sampling cartridges. Air samples collected on the Tenax® cartridges were thermally desorbed, using a Nutech® clamshell heater, onto a Nutech® model 8528 purge and trap system. The concentrated air sample was then desorbed, from the purge and trap into a Tracor® model 222, packed column gas chromatograph with flame ionization detection. The desorption sequence and gas chromatographic analysis sequence were controlled by a Perkin–Elmer® 7500 computer and Chromatographics 3® software. The Perkin–Elmer® 7500 system equipped with a LCI-100 integrator/printer supplied both a hard copy of the sample chromatogram and its analysis report (area counts and concentrations).

Mechanical performance testing

A series of 10, randomly ordered, test runs (including two replicates) were conducted at high and low setpoint conditions for each of the three environmental control parameters (temperature, relative humidity and airflow) controllable by the Test Facility. Acceptable performance of the Test Facility under each set of conditions was determined by calculation of the standard deviation from environmental condition setpoints based on 5-min averages for test durations of 8 h. Acceptance criteria of $\pm 1°C$, $\pm 10\%$ r.h. and $\pm 0.25\ \ell\ min^{-1}$ were used for temperature, relative humidity and ventilation airflows, respectively. These criteria were established considering manufacture specification of temperature, humidity and air flow instrument control limitations. Interactions among environmental control variables in the above test runs were determined using a 2^3 fractional factorial design (Hicks, 1982) using standard analysis of variance procedures. A commercially available computer program (SAS, 1982) was used to process test run data.

Organic recovery tests

Organic recovery tests were conducted using toluene and perchloroethylene additions (1) to quantify possible losses of these organics in the ETC and sampling manifold under various temperature, relative humidity, chamber mixing and ventilation airflow conditions, and (2) to determine if there were any interactions among the chamber conditions and observed recoveries. Again a fractional factorial, randomly ordered testing sequence was designed for subsequent analysis of variance.

Tests were conducted at 23 and 40°C, 40 and 60% relative humidity, and 1.3 and 6.2 $\ell\ min^{-1}$ (0.47 and 2.24 air changes per hour, ach) flow. For each test, environmental conditions were first established, then toluene and perchloroethylene

were introduced from a permeation oven into a mixing flask mounted above the test chamber at rates calculated to produce nominal concentrations of 200 and 400 $\mu g\,m^{-3}$, respectively. Hexane, the internal standard, was introduced from a separate permeation oven into a mixing flask located between the chamber and the sampling manifold. A test was begun after toluene and perchloroethylene reached expected equilibrium concentrations in the chamber. Sampling continued for a minimum of 4 h after each test was initiated. Samples were collected by pulling 1 ℓ of chamber effluent through glass cartridges packed with 1.6 g Tenax®. Sampling flow rate was controlled by Tylan® mass flow controllers which were calibrated by bubble flow meter. Collected organics were thermally desorbed at 190°C from the sampling cartridge to the concentrator trap of a purge and trap concentrator (Nutech Corp. model 8528). The concentrator trap, a 0.64-cm (1/4-in.) OD stainless steel tube 27.9 cm (11 in.) long and filled with Tenax® and charcoal, was then rapidly heated from room temperature to 190°C to desorb the concentrated sample to the column of the gas chromatograph, a Tracor® model 222 equipped with a flame ionization detector. A 10-ft, glass, 2-mm ID column packed with Carbopac B® coated with 1% SP1000 was used to separate compounds of interest. The gas chromatograph oven was operated isothermally at 200°C with a helium carrier flow of 30 cc per minute. Inlet and detector temperatures were maintained at 225°C.

The gas chromatograph response was calibrated by loading known amounts of hexane, toluene and perchloroethylene onto Tenax® cartridges and then desorbing the cartridges to the concentrator column of the purge and trap unit. Primary standards were prepared gravimetrically. Serial dilutions of the primary standard produced working stock solutions which were used for system calibration. These standards were refrigerated and remade weekly. The Tenax® cartridges were loaded by injecting 2 μl of working stock by solvent flush technique into the hot injection port of the purge and trap unit. A helium purge carried the volatized standard to the Tenax® cartridge through heated 0.16-cm (1/16-in.) stainless steel tubing. Loaded sample cartridges were then desorbed and concentrated using the purge and trap unit and analyzed with the Tracor® 222 GC.

Preliminary material emission testing

The purpose of the preliminary material test was to determine the emission rate changes of specific organic species and total organics for the test material. Tests were conducted under typical indoor environmental conditions of 23°C, 50% relative humidity, and chamber airflows of 1.0, 2.0 and 5.0 $\ell\,m^{-1}$ (0.4, 0.8 and 1.8 air changes per hour, ach).

Four materials were selected for initial material testing. The four materials were selected for their ability (1) to test the limits of the facility (both high and low emitters were used), (2) to test materials that contribute significantly to indoor air pollution according to other researchers, and (3) to allow some comparability with measurements made in other laboratories. Flooring glue and silicone caulking compound were selected as high emitters; foam carpet pad and particle board were selected as low emitters. Results from testing the flooring glue are presented and discussed. Work is in progress on the other materials.

A latex floor adhesive was obtained from a local commercial source. GC/MS headspace analysis was performed as described by Merrill *et al.* (1987) to provide guidance in selection of sample collection sorbent media, gas chromatographic column and calibration standards. It appeared from the headspace analysis that the bulk of emissions from the floor adhesive were C_6–C_9 hydrocarbons which were normal, branched, or cyclic alkanes and alkenes. Therefore, samples were collected on Tenax®, thermally desorbed to a 3.05-m (10 ft) glass 2-mm ID column packed with Carbopac B® coated with SP1000 and quantified using a flame ionization detector. The gas chromatograph was calibrated with hexane, heptane and *n*-octane, and an average response factor was determined which was used to reduce area counts, for all organics, to mass units. Primary standards were prepared gravimetrically from certified liquid calibration standards as described earlier.

In preparation for the initial material testing the emission test chamber was scrubbed with soap and water, triple rinsed with methanol and methylene chloride, and then rinsed with DI H_2O and dried. The test chamber was then placed back in line with the clean air system and purged at 5.0 $\ell\,min^{-1}$ (1.8 ach) overnight. Chamber background samples were taken to verify that there were no contaminant peaks greater than 10 $\mu g\,m^{-3}$ with retention times similar to compounds of interest emitted from the material.

The material test sample was loaded into the test chamber by removing the chamber from the incubator, reconnecting it to an auxiliary line of the clean air system, and then unbolting its top. The sample was then prepared and slipped into the chamber with the lid raised just enough to allow sample placement. This operation was done under positive pressure from the clean air system to keep intrusion of room air to a minimum.

The chamber was then sealed and pressurized to 1.5 psi. If the chamber leak rate was determined to be less than 1% of chamber volume per minute, indicated by a pressure drop of less than 1 psi in a 12-min period, then the seal was determined to be acceptable and the chamber was returned to the incubator and reconnected to the clean air system and sampling manifold. The mixing fan was set to 80 rpm, a rate calculated to move approximately 150 ℓ of air per minute. Environmental data collection was then initiated and sampling was begun after a 30 min equilibration period. The process of loading, pressure testing, and equilibration required about 1-1/2 h. Samples were taken every 1/2-h for the first 2 h, hourly for 4 h, and then at approximately 2-h intervals until the end of testing. Test termination was guided by observation of at least three chamber concentration measurements indicating a plateauing of the emission rate decreases.

The floor adhesive sample was prepared by spreading approximately 0.1 g adhesive onto one side of a 2.7-cm^2 aluminum plate that had been scrubbed with soap and water using a steel wool pad, then rinsed with methanol and methylene chloride and dried in an oven. Sample weight was determined by difference to the nearest 0.01 g. The sample was placed in the chamber within 5 min after weighing.

Sample volumes of 0.5–1 ℓ were collected during the high emission rate period of the emission test to prevent overloading of the concentrator column of the purge and trap unit and then increased to a maximum of 10 ℓ as emission rates decreased. Hexane was added to the chamber effluent from the permeation oven as a quality control measure. Duplicate samples were taken to confirm sampling reproducibility.

Temporal ETC organic concentration data are obtained from 9 to 14 integrated air samples for each material emission test run. Test runs were of 10–24 h duration. Emission rates presented later are estimated using Equation (5). The paper by Dunn (1987) applies non-linear regression analysis to the integrated air sampling concentrations data, derived from this study.

RESULTS

Mechanical performance testing

Tables 1 and 2 summarize the performance of the AEERL Emission Test Facility with regard to environmental control stability and an analysis of variance (ANOVA) for identifying possible control parameter interactions; i.e. control parameter dependencies.

Table 1. Results of mechanical performance test

Test run number	Temperature (°C) Mean	S.D.	Range	Relative humidity(%) Mean	S.D.	Range	Airflow (ℓ min^{-1}) Mean	S.D.	Range
MT 1	23.0	0	0.3	63.2	0.7	3.5	6.4	0	0.02
2	40.9	0.1	0.3	38.7	0.3	1.6	6.7	0	0.03
3	23.0	0	0	41.0	1.7	6.1	1.4	0	0.01
4	40.9	0.1	0	65.4	1.0	3.3	1.5	0	0.02
5	23.0	0	0	65.6	4.0	12.6	1.4	0	0.02
6	23.0	0	0	39.7	0.5	2.6	6.4	0	0.02
7	41.2	0	0	44.3	1.5	5.9	1.3	0	0.02
8	39.6	0.2	0.7	62.6	0.7	2.8	6.6	0	0.03
9	23.0	0	0	36.2	0.4	1.3	1.5	0	0.02
10	41.2	0	0	60.2	0.7	3.1	5.6	0	0.02

Table 2. Results from ANOVA evaluation mechanical performance test

Dependent variable	Source of effect	Significance probability ($PR > F_{III}$)
Temperature mean deviation	Humidity and airflow	0.26
Temperature mean square deviation	Humidity and airflow	0.32
Temperature range	Humidity	0.39
Humidity mean deviation	Humidity	0.24
Humidity mean deviation	Temperature and airflow	0.25
Humidity mean square deviation	Airflow	0.22
Humidity range	Airflow	0.06
Airflow mean deviation	Temperature, humidity and airflow	0.54
Airflow mean square deviation	Temperature	0.66
Airflow range	Temperature	0.15

Table 1 shows that the Test Facility (within the approximate operating ranges of 23–40°C, 40–60% relative humidity, and 1.3–6.5 ℓ min^{-1}) can hold setpoints for temperature within ± 0.1°C; for relative humidity within ± 2%, and for airflows within ± 0.7% of airflow readings. Note that this measured performance is quite near the limits inherent in specified instrument measurement accuracies and should also be evaluated in light of inherent analog to digital signal conversion limitations (Owens, 1982).

Table 2 is a selected summary of analysis of variance results in terms of significance probabilities for the most probable sources of effects on the listed dependent variable responses. The table shows that the significance probability (associated with the *F*-statistic) in all cases exceeds 0.05. This means that in all mechanical performance test runs, at the 0.05 significance level, the main and interactive source effects on the dependent variable are not significantly different than zero. Only in the case of the humidity range response does the significance probability approach 0.05, thus indicating that control of the Test Facility's humidity range response may not be independent of airflow setpoints. This analysis of variance based on the fractional factorial experimental design can only identify possible interactions in the control of the Facility environmental variables. Where interactions are identified and the control of environmental variables (i.e. temperature, humidity or airflow) is not adequate to ensure confidence in the use of experimental data (for example in predicting formaldehyde releases from wood products as a function of humidity), then the nature of the interaction will have to be defined and corrected.

Organic recovery testing

Table 3 presents the results of the organic recovery tests for the toluene and perchloroethylene chamber additions as well as the quality assurance internal standard addition of hexane. A consistent organic recovery performance for all three sampled organics is shown with no noticeable recovery biases.

The results in Table 4 were obtained from a fractional factorial analysis of variance on the Test Facility organic recovery performance data. The analysis of variance examined the effects of temperature, humidity, airflow and mixing (fan on or off) on the mean deviations of temperature, humidity, airflow, and on perchloroethylene and toluene recoveries.

The analysis of variance indicates there are no direct nor interactive effects of the Test Facility's environ-

Table 3. Summary of results of recovery performance test

Organic addition	Recovery (%) Mean	S.D.	Range
Hexane (internal standard)	104	5	93–109
Perchloroethylene	107	7	96–116
Toluene	98	8	88–109

Table 4. Results from ANOVA evaluation organic recovery test

Dependent variable	Source of effect	Significance probability ($PR > F_{III}$)
Humidity mean deviation	Fan	0.0400
	Temperature and humidity	0.0451
	Temperature and airflow	0.0093
	Airflow	0.2976
Airflow mean deviation	Humidity	0.0124
	Airflow	0.0051
	Fan	0.0047
	Temperature and humidity	0.0102
	Temperature and airflow	0.0184
Perchloroethylene recovery	Airflow	0.1337
	Temperature and airflow	0.2269
Toluene recovery	Airflow	0.0837
	Temperature and airflow	0.2367

mental control variables on toluene or perchloroethylene recoveries through the Facility's emission test chamber and sampling manifold. This result coupled with the percent recoveries reported in Table 3 supports the applicability of the zero pollutant loss rate assumption made in the simplification of the mass balance Equation (1).

A rather disconcerting though non-critical result of the fractional factorial analysis of variance for the recovery test performance data is the number of direct and interactive effects which were identified as significantly affecting humidity and airflow mean deviations. This is explicable in an academic sense because of the independence of the mechanical performance and recovery tests but is not intuitively obvious especially considering that temperature, humidity and flow control performances for the recovery tests were characterized by comparable set point standard deviations to those shown in Table 1 for the mechanical tests.

Material testing results

Figures 2 and 3 show the temporal test chamber concentrations of both octane and 'total organics' (normalized for sample mass) that were observed during the emissions rate characterization of a water-based floor adhesive. These plots represent two simultaneous processes: the change in emission rate as the material ages and ventilation of the emissions that built up in the chamber during pressure testing of the chamber seal.

Table 5 presents calculated total organic emission rates for four samples of a floor adhesive tested in the emissions test facility. Three of the samples were small, approximately 0.1-g samples. Chamber concentration

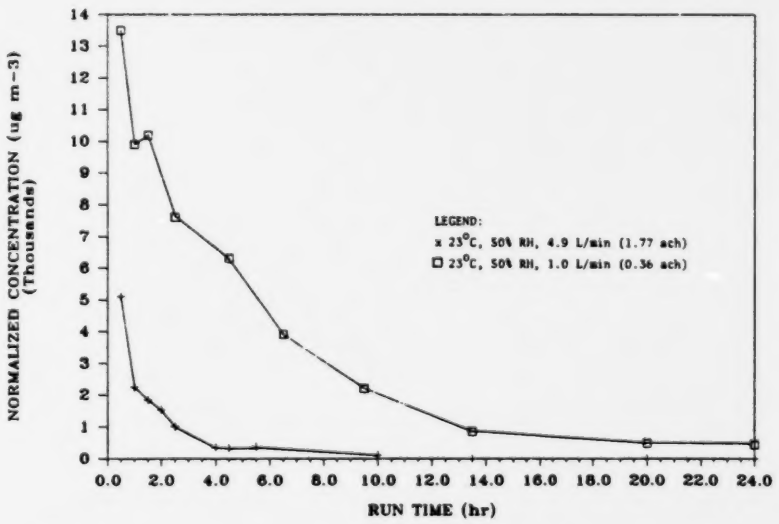

Fig. 2. Emission test chamber total organics concentration vs time floor adhesive No. 1.

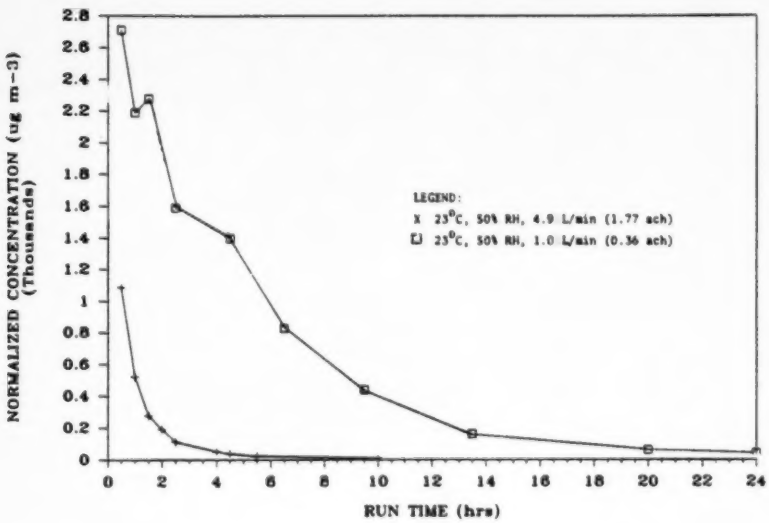

Fig. 3. Emission test chamber octane concentration vs time floor adhesive No. 1.

Table 5. Calculated emission rates for water based flooring adhesive

Run ID	Airflow (ℓ min^{-1})	Air changes (ach)	Specimen age	Emission rate (mg m^{-2} h^{-1})	(μg gm^{-1} h^{-1})
AD 1.1.2	4.92	1.77	10 h	37	210
AD 1.1.3	4.92	1.77	10 h	35	282
AD 1.3.2	1.00	0.36	24 h	29	259
AD 1.4.1	4.92	1.77	11 day	< 0.08	< 0.6
Mølhave *et al.* (1982)	0.69 (1 acd)	0.04	8–14 day	271.0	—
Girman *et al.* (1984)	Vacuum extraction	—	14 day	—	610–780*

* Total alkanes.

vs time curves are shown for samples AD 1.1.2 and AD 1.3.2 in Figs 2 and 3. Sample AD 1.1.3 was a replication of test AD 1.1.2. Sample AD 1.4.1 (24 g) was conditioned outside of the test chamber, under a laboratory hood for 11 days, and then examined under the 4.92 ℓ min^{-1} test condition.

The results of Mølhave *et al.* (1982) for one water-based floor adhesive and of Girman *et al.* (1984) for several different water-based adhesives are included in Table 5 for comparative purposes. This comparison shows some correspondence of emissions factors calculated under widely differing test conditions but emphasizes the need to establish comparable sample aging or conditioning and testing methodologies as well as standardized reporting of results.

Figure 4 is a typical chromatogram, depicting FID detector response to compounds collected by concentration of 1 ℓ of chamber effluent onto Tenax® 4 h after initiation of test AD 1.3.1. Seven of the major compounds shown in Fig. 4 accounted, on average, for about 60% of total chromatographed organics for the four small sample floor adhesive tests. *N*-octane averaged 17% of observed organics and was generally highest in concentration. Compounds not readily thermally desorbed from Tenax® were not observed in GC/MS headspace evaluation; therefore, sampling for compounds beyond the Tenax® window with XAD-2 resin was not pursued (Merrill *et al.*, 1987).

Five sets of duplicate samples were collected. Reproducibility, expressed as the difference between duplicates divided by the mean, averaged 5.4% for hexane (the internal standard) and 10.4% for total chromatographed organics for four of the five pairs of collected samples: one set exhibited a > 50% difference in response, indicating a leaking or cracked sample collection device. Recovery of the internal standard averaged 100.6 ± 22% for all samples analyzed. Chamber background was 20 ± 10 ng ℓ^{-1} for

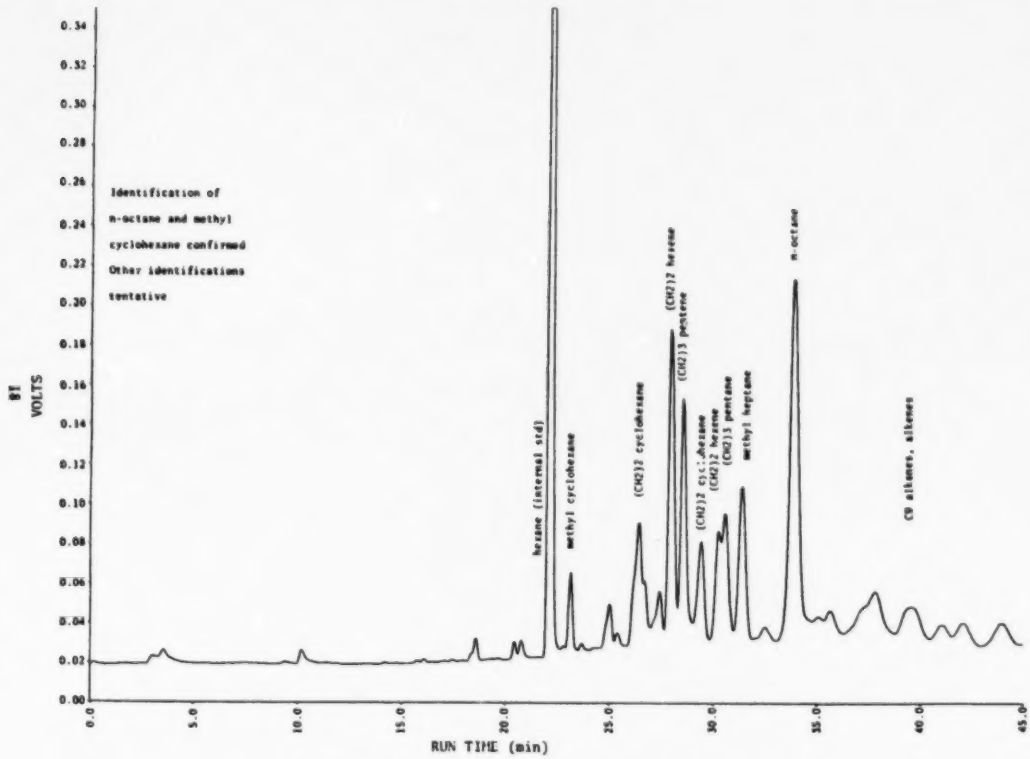

Fig. 4. Typical chromatogram for water-based adhesive.

two 10-ℓ blanks and $10 \pm 10\,ng\,\ell^{-1}$ for a 5-ℓ sample. Background contamination collected on 1-ℓ chamber blanks was below the method detection limit.

CONCLUSIONS

Based on the monitored performance of approximately 20 preliminary runs of 6–8 h duration at environmental conditions of 23–40°C, 1.3–6.5 ℓ min^{-1}, and relative humidities of 40–60%, the AEERL Emission Test Facility can hold environmental conditions within extremely close tolerances; viz., temperature ± 0.1°C, relative humidity ± 2.0%, and airflow ± 0.7% of airflow readings. Considering other uncertainties, inherent in general organic emission characterization studies, limited attention needs to be given to intervention in the environmental control and monitoring aspects of the current Emission Test Facility operation.

A general characterization of the overall performance of an emission testing system such as the AEERL Test Facility with regard to environmental control stability and organic recovery efficiencies is an essential quality assurance and quality control aspect of any emission characterization project.

Recoveries of organic species through the emission test chamber, sampling manifold, and adsorbent sampling system which ranged from 88 to 116% with standard deviations between 5 and 8% may be marginally acceptable for the purpose of determining time specific test chamber concentrations or material emission factors. Data of such quality as part of definition of an emission rate process may be quite acceptable, however, since definition of the emission process and model development will rely on statistical regression (curve fitting) techniques.

In order to ensure quantitative comparability of emission factor or rate determinations for a specific material, in addition to (1) control of sample conditions, (2) initiation of emissions sampling with minimum time delay, (3) precise and accurate control of material test environmental (temperature, relative humidity, airflow, mixing) conditions, and (4) operation of an analytical system which allows for quantitation and identification over a wide range of organic compounds, study protocols should address (5) sample acquisition and storage conditions, (6) the physical characteristics of the test sample as they may affect mass transfer through the sample, (7) precise and accurate characterization of test sample mass and surface area parameters, and (8) determination and

control of sample surface to test chamber volume ratios.

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